

**Preliminary Investigation into the Corrosion of
Beryllium Exposed to Celotex and Water**

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Executive Summary

Ion chromatography of Celotex packing material performed by Lawrence Livermore National Lab (LLNL) has revealed that this material contains aggressive anions which may accelerate corrosion¹. Specifically, 0.944g Cl⁻/kg Celotex and 0.125g F⁻/kg Celotex. While it has been demonstrated that Cl⁻ causes pitting type corrosion of Be², it was uncertain in the LLNL work if accelerate corrosion would result when beryllium was exposed to Celotex and moisture.

This investigation attempts to evaluate the potential risk of accelerated Be corrosion from Celotex and water (that may occur naturally from Celotex dust and moisture from the atmosphere). To accomplish this, a sample of Celotex was ground and then soaked in a volume of deionized water for several weeks. The resultant supernatant solution was extracted and used for Be corrosion experiments.

Potentiodynamic polarization curves for Be in the Celotex solution found that Be suffered from pitting type corrosion at its open circuit potential. When the pitting potential of Be in the Celotex solution was compared to the theoretical pitting potential for Be in $3.0 \times 10^{-3} \text{M Cl}^-$ (as calculated from the LLNL data), the pitting potential for Be in the Celotex solution was more negative than the theoretical value. However, IC analysis of the Celotex solution prepared for this investigation revealed a far higher concentration of Cl⁻ than calculated from the LLNL data. When actual Cl⁻ concentration determined from the IC analysis was used to establish the theoretical pitting potential for Be in the Celotex solution the two pitting potentials compared well. In the analysis of Celotex, the concentration of Cl⁻ was 1.8g Cl⁻/kg Celotex. For 20 lbs.(9.1 kg) of Celotex there is a *minimum* of 16.2g of extractable chloride. The actual amount is likely higher. Similar IC analysis for F⁻ revealed that its concentration was 0.9g F⁻/kg Celotex. The difference between the LLNL and LANL analysis of the Cl⁻ concentration most likely owes to the duration which the ground Celotex was allowed to soak prior to using it in the corrosion experiments. In the LLNL IC analysis the large pieces of Celotex were only allowed to soak in solution for 2 hours. In the LANL analysis, the Celotex was ground into small pieces and allowed to soak in solution for approximately 3 weeks.

Microbial, analysis of the Celotex solution found a high concentration of the bacteria diptheroids bacillus. This bacteria is an slow growing air borne species that are commonly found. The high concentration of diptheroids found in the Celotex solution, however, indicates that the bacteria is able to grow nutrient in the Celotex water. Currently we are examining whether or not diptheroids bacillus increases the corrosion rate of beryllium.

While preliminary, these results indicate that storage conditions which may expose Be to a combination of Celotex and moisture will result in pitting type corrosion of the Be. Currently we are investigating the exact atmospheric conditions (i.e. temperature, humidity, Celotex dust levels) which will result in the pitting corrosion of Be. These studies are being carried out in an atmospheric corrosion testing chamber to simulate storage conditions. Further studies on the effect of the other constituents in Celotex are being carried out in the laboratory.

¹ "Extraction Analysis of Celotex Packing Material", James D. LeMay, Lawrence Livermore National Laboratory, April 14, 1995.

² M.A. Hill, R.S. Lillard, D.P. Butt, "Corrosion / Electrochemistry of Beryllium and Beryllium Weldments in Aqueous Chloride Environments", LA-UR# 97-116, Los Alamos, October 1, 1996.

Experimental Methods

The Celotex packing material analyzed in this investigation was composed of approximately 80 wt% sugar cane fiber 10% paper and 10% starch. The original specifications call for a grade of material which complied with ASTM C208 and C209. In order to obtain a sufficient amount of liquid to run a polarization curve and to insure a much of the water soluble components in Celotex were extracted, 111 grams of Celotex were soaked in 700 ml of twice distilled deionized water for approximately three weeks. A Buchner funnel was used to extract the supernatant liquid from the Celotex. Of the original 700 ml of water, 250 ml was extracted and subsequently diluted with 125 ml of deionized water to yield a total of 375 ml of liquid. The pH of this solution was 4.0. Approximately 370 ml of this was used for electrochemistry experiments. This solution was deaerated in high purity argon for three days prior to immersing the sample. The remaining 5 ml of solution was analyzed for chloride and fluoride using ion chromatography (IC). To facilitate the IC analysis, the solution was diluted prior to analysis (1 part solution to 10 parts deionized water).

Potentiodynamic polarization curves for Be in the Celotex solution were run at a scan rate of 0.1 mV/sec. A 5.3 Hz low pass filter was used to minimize noise. A saturated calomel electrode (SCE) was used for the reference electrode and a platinum mesh for the counter electrode. The S200F beryllium working electrode had a surface area of 1.43 cm² and was polished with 400 grit SiC paper prior to testing. Electrochemical measurements were made using an commercially available hardware and software. To insure steady state, samples were left at there open circuit potential for one hour prior to running the polarization curves.

Results and Discussions

The Lawrence Livermore National Laboratory (LLNL) IC analysis of Celotex found that the concentration of Cl^- was 0.94g / kg Celotex. Therefore, the amount of chloride in the Celotex sample after soaking was:

$$(0.111 \text{ kg Celotex})(0.944\text{g Cl}^-/\text{kg Celotex})= 0.105\text{g Cl}^-$$

The initial chloride concentration in solution was equal to:

$$(0.105\text{g Cl}^-)/(0.700\text{L})(1\text{mol}/35.5\text{g Cl}^-) = 4.2 \times 10^{-3}\text{M Cl}^-$$

However, only 0.250L of this solution was diluted with 0.125 of deionized water giving a final concentration of Cl^- in the test solution of:

$$(0.250\text{L})(4.2 \times 10^{-3}\text{M Cl}^-)(1/0.375\text{L})=2.8 \times 10^{-3}\text{M Cl}^-$$

Similar calculations from the LLNL data found that the F^- concentration in the Celotex solution to be $2.9 \times 10^{-4}\text{M}$.

To determine the precise concentration of Cl^- and F^- in the Celotex solution IC analysis was performed here at LANL on the 5 mL aliquot removed prior to testing the Be. The actual chloride concentration of the solution was determined to be 0.008 M as compared to the 0.0004 M concentration as determined from the calculation using the LLNL analysis. From the LANL analysis of Celotex, the Cl^- was determined to be 1.8g Cl^- /kg Celotex:

$$(0.008\text{mole Cl}^-/\text{L})(0.700\text{L})(35.5\text{g Cl}^-/\text{mole})(0.111\text{kg Celotex})^{-1} = 1.79\text{g Cl}^-/\text{kg Celotex}$$

For 20 lbs.(9.1 kg) of Celotex there is a *minimum* of 16.2g of extractable chloride. The actual amount is likely higher. Similar IC analysis for F^- revealed that its concentration (in terms of Celotex) was 0.9g F^- /kg Celotex. The concentration of F^- in the solution would therefore be 0.007M. The Celotex solution was also tested for the presence of microbes. It was determined that the bacteria diptheroids bacillus was present at higher concentrations than those found normally in the lab. While it has not been determined if the bacteria originated in the Celotex, it is almost certain that their ability to reproduce was aided by the nutrients found in the Celotex. Namely the sugar cane.

The difference between the Cl^-/F^- concentrations determined in the LLNL IC analysis of Celotex and those determined here likely owes to the differences in the extraction methods. Here the Celotex was shredded into small, 2-0.5 cm pieces, and allowed to soak in solution for approximately three weeks prior to use. In the LLNL method, the sample sizes were 5-10 grams and no mention of grinding/shredding the Celotex was reported. Further, the samples were only allowed to soak in solution for 2 hours prior to IC analysis. Therefore, it is likely that the smaller particle sizes and longer soak times allowed more of the free available chloride to dissolve into solution.

The open circuit potential (OCP) as a function of time for S200F Be in the deaerated Celotex solution is presented in Figure 1. As the OCP rises to -0.850 V SCE, transients in the potential time curve not observed at lower potentials begin to appear. These potential / time transients at longer immersion times are an indication of pitting corrosion.

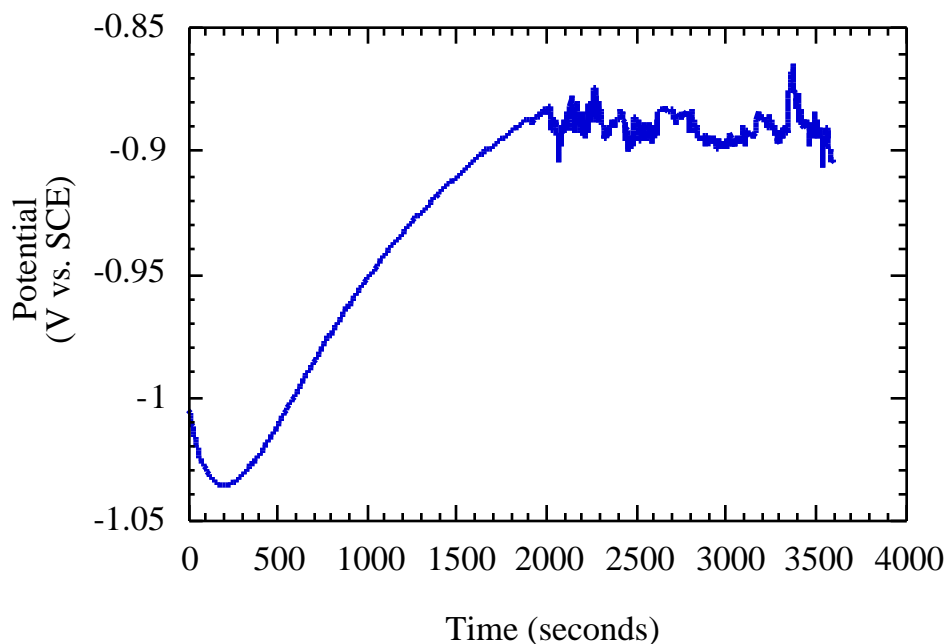


Figure 1 Open circuit potential as a function of time for S200F Be in Celotex solution.

A typical potentiodynamic polarization curve for Be in the Celotex solution is presented in Figure 2. For comparison, a polarization curve for Be in 0.01M NaCl is presented in Figure 3. For Be in 0.10M NaCl solution pitting corrosion is observed at potentials above -0.950 V vs SCE. This is the pitting potential for Be in 0.01M NaCl. It is characterized by large changes in the current density for very small changes in the applied potential. Upon removing this sample from the chloride solution large corrosion pits were observed. For Be in the Celotex solution, large changes in the current density were measured for very small changes in the applied potential at all potentials above the OCP (Figure 3). Once again, this response is typical for materials which are susceptible to pitting corrosion in this environment. Upon removing the Be from the Celotex potential for Be in a solution containing 0.008M chloride (the concentration found in the Celotex solution) is -0.865V vs SCE (see equation in Figure 5). This value compares well with the observed pitting potentials of approximately -0.850V and -0.870V vs SCE and the theoretical curve in Figure 5. However, the theoretical pitting potential calculated from the LLNL Cl⁻ concentration analysis does not compare well with the measured pitting potential. As shown in Figure 5, the values predicted from the LLNL analysis are approximately 50 - 75 mV more negative than the observed pitting potentials for Be in Cl⁻. More negative values are consistent with an underestimation of the Cl⁻ concentration.

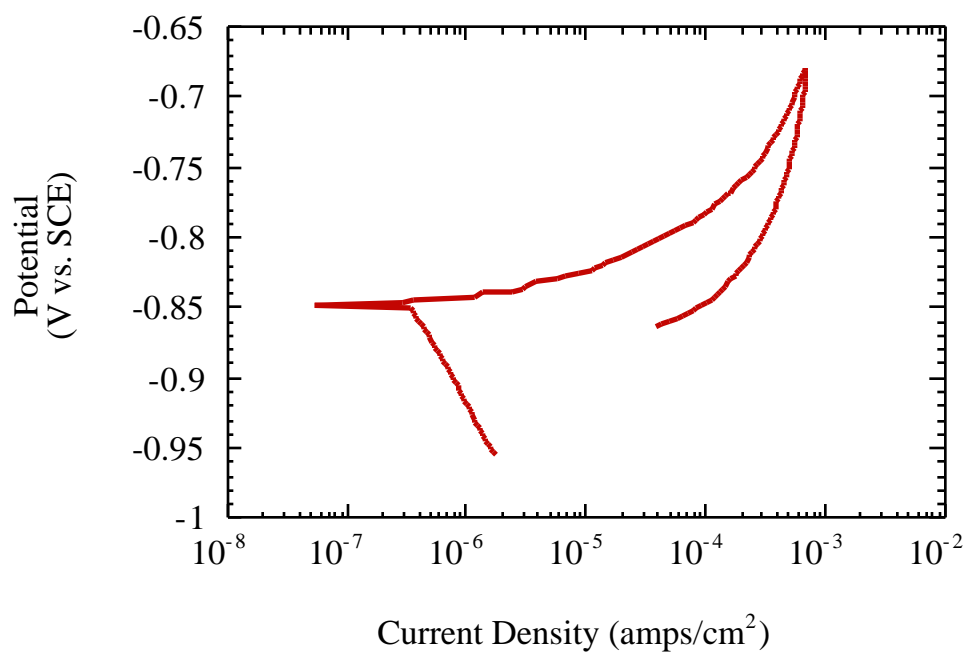


Figure 2 Potentiodynamic polarization curve for S200F Be in Celotex solution.

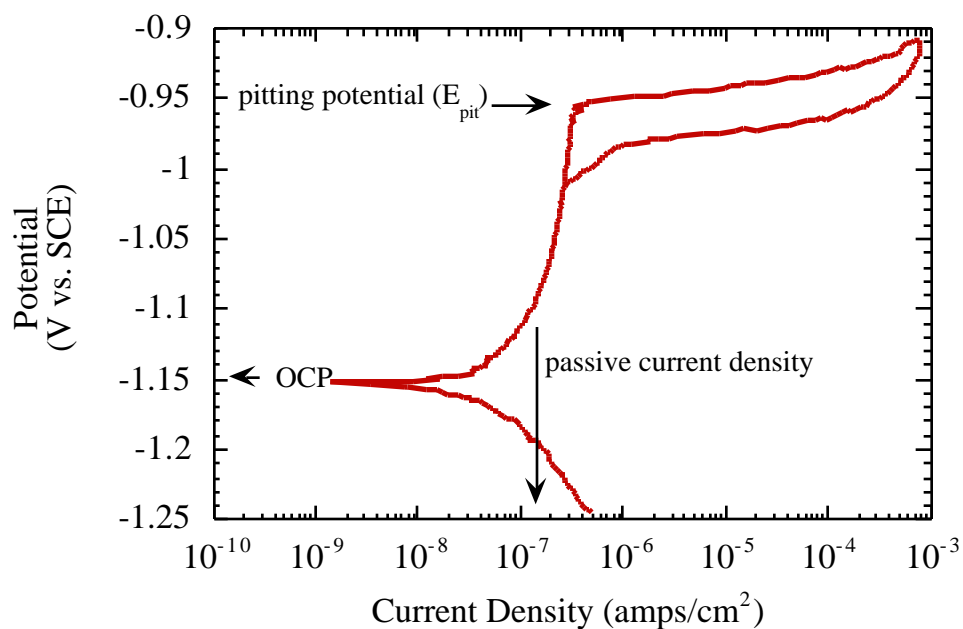


Figure 3 Potentiodynamic polarization curve for S200F Be in 0.10M NaCl

Figure 4 Photo-micrograph showing corrosion pits in Be S200F after polarization in Celotex solution.

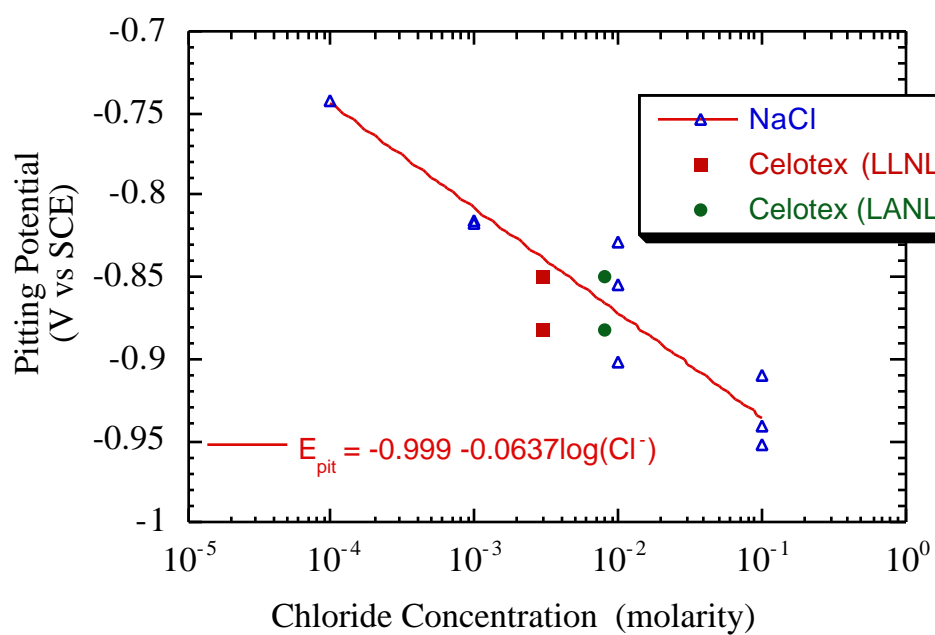


Figure 5 Pitting potential for Be S200F as a function of chloride concentration. Measurements made in deaerated NaCl at ambient temperature. Graph also presents pitting potential observed in Celotex solution based on LLNL calculation of chloride concentration and LANL.

Conclusions

These results indicate that storage conditions which may expose Be to a combination of Celotex and moisture **will** result in pitting type corrosion of the Be.

It is important to note that this brief report has not attempted to address the effect of other constituents in the Celotex on the corrosion of Be. Specifically the presence of fluoride and diptheroids bacillus. Fluoride is known to cause pitting corrosion in aluminum and other materials. There is no reason to suspect that Be is immune from F^- attack. Moreover, given the fact that Be is less resistant to pitting attack from Cl^- than Al, there is every reason to suspect that Be will suffer from pitting corrosion in F^- containing solutions. Currently we are investigating the effect of these constituents and the exact atmospheric conditions (i.e. temperature, humidity, Celotex dust levels) which will result in the pitting corrosion of Be.